

## 13.0 Function-Integrated Materials

### 13.1 Introduction

#### The Nature of Function-Integrated Materials

The technological selection of materials commonly targets a given collection of properties which define the materials' primary function in a system. For example, in an Air Force context, carbon-epoxy composites on an aircraft serve a structural function and are selected because they offer a good compromise on low density, high stiffness, and high strength. Piezoelectric materials, on the other hand, are not usually selected for a structural function but for their ability to perform mechanical-electrical energy transduction with high efficiency. The materials of optical fibers are selected of course because of their light transmission properties, but they do not have ideal mechanical flexibility and repair processability. Materials as we know them and use them at the present time are largely monofunctional. Many materials-enabled technologies can be envisioned for the future through synthesis of structures in which multiple functions are integrated by molecular design in one material. The best examples of function-integrated materials by design are in fact found in biology, and they remain generally an unrealized vision in technology.

The vision for function-integrated materials would be materials in which sensing functions using photons, mechanical forces, and magnetic or electric fields are built into the molecular structure within the boundary conditions of a secondary or even tertiary function related to structure or ability to interconvert energy. Such binary and ternary combinations of a material's functions by structural design has not really occurred technologically. A possible application of such materials in Air Force systems would be sprayable and adhesive batteries or solar cells for the wings of aircraft to convert solar energy to electrical power and store it, all while at high altitudes. These sprayable batteries would be, ideally, composite structures that have the processability of currently known materials and even have load-bearing capacity. Another relevant application would be sprayable, structural composites which have a switchable antenna function to receive and process information or be stealthy on demand. The concept can be extended to sprayable materials for tunable radomes and special sensors. To close the loop on function integration, the new materials that should be explored must be potentially recyclable. This is important not only for environmental purposes but also because function integration in materials will enable technologies at a cost. An extremely promising and unexplored group of materials for function integration are nanophased organics and nanophased composites.

#### Nanophased Metals and Ceramics

The materials community worldwide recognizes nanophased materials as one of the important frontiers for materials technology. Research on nanocrystalline metals and ceramics was initiated during the past two decades, and many potential opportunities have been identified. For example, superplasticity has been observed in nanocrystalline ceramics such as alumina. Another important property identified in laminated ceramic-metal nanostructures has been extremely high dielectric constant. Nanostructured ceramics could also play a very important role as thermal barriers in airframe and propulsion applications. A general advantage that could

be achieved in nanocrystalline metals and ceramics is high purity, which may be important in enhancement of mechanical properties. The properties of nanocrystalline intermetallics are still not very well known; this is due in part to the limited scale up of these materials to date. Nanocrystalline metals and ceramics could be important in Air Force technologies since they could play a key role in the development of higher temperature engines or other aircraft components. Ceramic-metal nanophased materials could also lead to new materials with super dielectric constants. This would enable a technology of highly efficient, miniaturized antenna arrays on air vehicles.

## **13.2 New Directions in Function-Integrated Nano-Structured Materials**

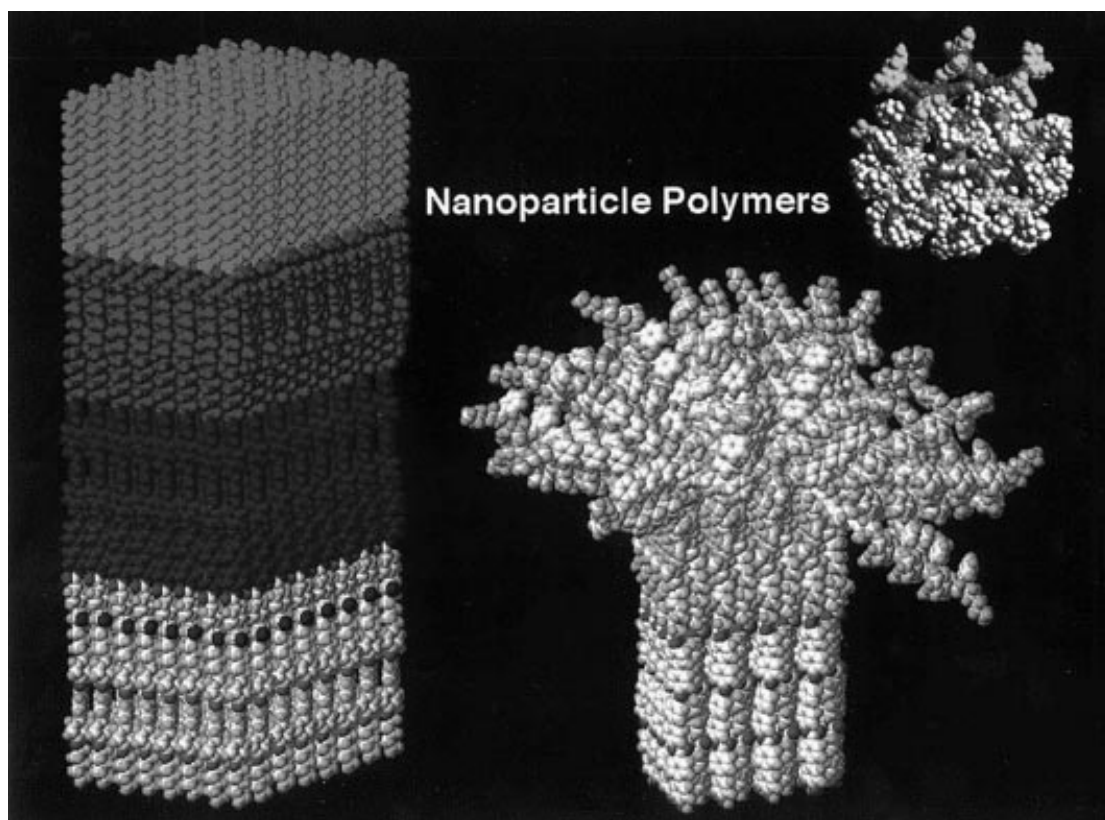
### **Nanophased Polymers**

Relative to metal and ceramic nanostructured materials, little is known about the properties of nanophased polymers and organic-inorganic nanocomposites. In the field of polymers, considerable attention has been given over the past two decades to microphase separated materials. These materials consist of block copolymers in which chemically different segments have fairly narrow distributions of molar mass. At equilibrium these polymers self-organize into microstructures with various geometries. However, ordering occurs very slowly or requires applied shear forces to increase the rates at which they order. These include, for example, lamellar structures, cubic superlattices, hexagonal phases in which similar segments segregate into cylindrical structures, and several bicontinuous structures which have been discovered more recently. The properties of these microphase separated polymers are still being investigated, however, common flexible copolymers require rather high molar mass to exhibit a thermodynamically stable microphase separated state. Thus, it will not be easy to make the transition into nanophased organics with common block copolymers. Special polymers with rigid segments or special molecular architectures will be required to truly access the nanometer regime. Furthermore, for certain applications it would be important to develop nanophased polymeric materials in which the nanostructures consist of single macromolecules and also have distinct shape. This concept is referred to here as “nanoparticle polymers” and is described in further detail later in this section.

If the Air Force had access to nanophased polymers, various technological quantum leaps related to materials could occur. These include ultralight materials for structural applications which may not require carbon fibers, glass fibers, or ceramic particles for reinforcement, materials recycling technologies, as well as the function-integrated materials described above. Certain molecular structures in nanophased organics could also be used as recyclable paints and adhesives. Nanophased polymers would also be important to Air Force technologies because such structures might be necessary to produce stable third-order nonlinear optical materials that utilize high-amplitude photons to transmit, process, and store information at rates several orders of magnitude faster than currently possible. These materials could serve as optical computers on air vehicles and being organic or composite in nature would not add significantly to the weight of aircraft, satellites, missiles, or rockets. Relative to silicon-based computer technologies, information processing with photonic organics is projected to be 10,000 times faster.

Solid energetic materials that would be molecularly designed to have nanometer or micron sized regions of all key ingredients is one additional outcome from nanophase polymers. The vision in this concept would be to generate the ability to design single-component solid propellants and explosives processable as macroscopically ordered structures. For example, energetic materials could be produced with nano- or micro- tubes of oxidizer in fuel matrices, oriented in a common direction within a charge. Alternatively, layered structures could be formed by self-assembly of a fuel-oxidizer block copolymer. Again, the structural chemistry or architecture of blocks would be key in achieving nanometer as opposed to micron sizes in structures. Such materials could bring spatial control of focused energy, homogeneous energy dissipation and safety, as well as enormous increments in specific impulse.

*Nanoparticle Polymers: Processing and Recycling via Reversible Sintering, Molecular Nano-Composites.* The polymeric materials of contemporary technologies contain long chain macromolecules which are typically coiled in solution or in the melt. When solidification occurs, these long molecules either fold if they crystallize or extend under flow when fibers are



*Figure 13.1 Molecular Graphics Rendition of Nanoparticle Polymers with Dimensions on the Order of Several Nanometers*

produced. Missing among the large number of polymeric materials available today are materials composed of polymer molecules that resemble hard particles with nanoscale dimensions. The analogy to hard particles is based on the concept that such polymer molecules would have a well defined shape that never changes as materials transform from liquids to solids and vice versa. Such materials could be appropriately described as molecular object polymers or nanoparticle polymers and would have shapes generated irreversibly through covalent bonds. Figure 13.1 shows a molecular graphics rendition of three structures which could be considered nanoparticle polymers. In essence, nanoparticle polymers would be polymers that resemble nanocrystalline ceramics. The actual structures shown have been synthesized in academic materials chemistry laboratories but not yet in a scale large enough to allow a thorough investigation of their technological potential.

With technological access to nanoparticle polymers, we could revolutionize the nature and the processing techniques of lightweight, high-strength materials. For example, nanoparticle polymers could be sintered the way ceramics are sintered, except that this would be possible easily at very low temperatures and could involve reversible secondary bonds or ionic bonds. This process of organic sintering could be controlled by surface chemical modification of the nanoparticle polymer molecules. Most importantly, there is the opportunity to develop the concept of reversible sintering which should be of great importance in a recycling context. Desintering of macroscopic structures into nanoparticles could occur at temperatures slightly higher than those used in the original sintering process or by resuspension of the nanoparticles in water when ionic bonds are used as a means to sinter the macroscopic structure. Nanoparticle polymers would have by definition a covalent structure somewhat similar to that of crosslinked polymers, given that their molecular shapes would be sustained by a covalent structure. Crosslinked polymers, including the epoxy matrices of composites, as well as rubbers, cannot be recycled by solvation or melting. In this context the possibility of efficiently processing and recycling nanoparticle polymer materials is an exciting prospect. The final materials processed from nanoparticle polymers could take morphological forms that would resemble, for example, stacked and glued mica-like organic flakes or densely packed and oriented organic fibers of nanoscale diameter. One of the characteristics of such materials would be very high strength-to-density ratios, but many other novel properties could be imparted to the structures through molecular design of the nanoparticle.

Using a nanoparticle polymer technology, novel molecular composites could emerge for high-strength, lightweight airframe components. Such materials could use nanoparticles as the reinforcement, but use conventional polymers as the binding matrices. This would introduce additional degrees of freedom in tuning properties, since stiffness could be controlled through the nature of the matrix, and possibly property anisotropy and strength through the nanoparticles and their anchoring chemistry to matrix materials. Recycling for materials formulated as molecular composites could involve simply the depolymerization of very small quantities of conventional linear polymers serving as the interparticle glue. In these materials, as suggested before, crosslinking would be totally internal to the nanoparticles and therefore would not interfere with recycling as it does now in advanced composites based on epoxy matrices.

Work is starting in laboratories throughout the world to produce macromolecular structures that resemble hard nanoparticles two or more orders of magnitude larger than buckyballs. The magnitude of the effort is still very small, but most importantly ongoing work does not

necessarily envision the role of such macromolecular structures in advanced materials. Therefore, the possible revolution they could contribute to processing, recycling, and function integration in materials is really not part of the current vision. Research programs are needed that will target macromolecular particles as the components of advanced materials.

*Nanophased Polymers and Damage-Resistant Electronic and Photonic Organics.* Organic materials with conjugated structures can exhibit many useful properties for advanced technologies. These properties include third-order nonlinear optical properties, electrical conductivity, electroluminescence and photoluminescence among others. All of these properties are important for sensor development or energy conversion functions in materials. However, the problem with such materials is the fact that many electronically delocalized organic structures can be chemically unstable or have poor resistance to laser beam damage. Conjugated structures also tend to aggregate due to interactions such as carbon-carbon overlap, and this may significantly quench some properties. Strategies to protect these structures through molecular encapsulation need to be investigated, and this is where nanophased polymers of the nanoparticle type may play an important role. Specifically, it may be possible to design nanoparticles in which internalized delocalized structures are protected by robust molecular shells. This would also facilitate the processing of electronic and photonic organics using the sintering methodologies described above.

The role of molecular architecture in the effective encapsulation of conjugated structures needs to be investigated. Specific examples could include the use of dendrimeric structures or layered particles of various shapes of dimensions smaller than those of the wavelengths of interest in order to avoid scattering. In cases where long-range electronic conduction is desired, the encapsulation of the most sensitive conjugated structures needs to involve conducting shells, hopefully damage-resistant ones. Future optical computing sensing devices, and laser beam protection devices would benefit from a nanophase approach to the protection of environmentally sensitive structures.

## **Nanoparticle Polymers and Function-Integrated Materials**

The potential of nanoparticle polymers in function-integrated materials is based on the possibility of designing molecularly two or more functions in the nanoparticle. For example, one could combine a sensing function, an energy transduction function, and a structural function in a given nanoparticle. Conventional polymers considered for second order nonlinear optics are entangled linear chains which have to be mixed with dye molecules and then poled in an external electric field in order to make an electro-optical sensor device. On the other hand, if the basic unit of the sensing material is the anisotropic plate nanoparticle, dye molecules could be pre-incorporated covalently inside the plate in a given orientation relative to local coordinates of the nanoplate. The macroscopic orientation needed to make the sensor would arise from the polar macroscopic stacking of plates. In addition to the sensing function, the nanoplate is also a useful structural element offering stiffness and planar anisotropy. Structurally, one could say that the nanoparticle is a microstructural unit cell of the material since its structure reflects the final microstructure and anisotropy of the macroscopic solid. A good case in point is the structural similarity between the anisotropic nanoparticles that resemble plates and the macroscopic material produced when the plates are condensed with a common stacking direction.

## **Nano-Composites: Molecular Dispersion of Organics in Semiconductors, Metals, and Ceramics**

The composite materials that emerged over the past few decades and used presently in Air Force systems are mechanical mixtures of two or more components, typified by the dispersion of fibers in a polymer matrix. The performance and processing of these systems will probably continue to improve but many limitations will remain with regard to recycling, cost, and repair of structural components. Little is known at present about the properties that may emerge if organic molecules, including polymers, could be dispersed molecularly in ceramic or metallic lattices. In nature, for example, molecularly dispersed proteins toughen extremely brittle ionic lattices to a point where ductile fractures are observed. A good example of this phenomenon is biogenic calcium carbonate.

Research is proceeding in the U.S. and elsewhere on the intercalation of polymers in ceramic materials. For example, work is being carried out on the intercalation of both hydrophilic and even hydrophobic polymers in layered inorganic solids such as silicates and calcium aluminates. These materials have been shown to have enhanced mechanical properties such as higher toughness or compressive strength. The intercalation of the organic in these layered inorganics produces lamellar ceramic-polymer nanocomposites. Most of the synthetic methodologies are direct, that is, they involve diffusion of polymers between inorganic layers. Precipitation of the inorganic component from concentrated polymer solutions has also been explored as a different approach to intercalation and offers distinct advantages. In this case the precursor ions to the inorganic solid are dissolved in the polymer solution.

The precipitation of inorganic materials in organic media needs to be investigated further, including precipitation in ordered media. One of the interesting aspects of the precipitation approach is the possibility of having a liquid or viscoelastic precursor to the nanocomposite which would be of great importance in processing. Also, the precipitation approach could produce interfacial bonding between the nanophases through the possibility of molecularly dispersing the organic component in the inorganic lattice. This last issue also impacts our ability to design novel properties by close coupling of the nano-phases. Other possible avenues to produce interesting nanocomposites would be to explore the simultaneous spraying of metals and polymers on substrates.

Synthetic examples of nano-composites could offer not only novel mechanical properties, but also unique electrical, optical, and transport properties at weight ratios of organic and inorganic content which are not common in conventional composites. Novel electrodes and corrosion-resistant metals with relatively little organic content are additional examples of systems that could emerge from these materials. Molecular level dispersion of organics in inorganic materials also opens the possibility of finding thermodynamically stable composite materials; this is of obvious consequence to recycling of composites. In many instances, primarily in soluble materials, the composite solid state would reform spontaneously, thus offering facile recycling of high-value-added materials. The prospects for this area of advanced materials are promising, but this field will only develop through the interdisciplinary efforts of organic chemists, inorganic chemists, and materials scientists.

## **Nano-Composites and Function-Integrated Materials**

Innovation in nanocomposites brings the potential for novel classes of function-integrated materials. One possibility is the creation of processable materials with energy storage functions coupled to structural functions. In the precipitation approach mentioned above, an organic matrix would be used as the precursor for nucleation of a nanostructured semiconductor that behaves as a solar cell. The precursors to these nanocomposites could be sprayable substances that are deposited on external or internal surfaces of air vehicles. After spraying, semiconductor nanophases could grow through vapor infiltration of a reactant or through changes in temperature. Synthetic routes of this type have been tried in laboratory scale and demonstrated to be feasible in principle. A possible technology to emerge from this would be composite structural coatings that can behave as solar cells and energy storage devices, an important technology for an aircraft that can orbit at 100,000 feet.

## **Superlattice Molecular Materials**

A closely related concept to nanophased polymers and composites which is not equally recognized as a possible frontier for advanced materials, is that of superlattice materials. Such materials, fully organic, inorganic, or organic-inorganic composites would consist of molecular clusters a few nanometers in size that self organize into large superlattice arrays. An example of a superlattice molecular material is the colloidal array. Synthesis of highly charged, monodisperse colloidal arrays from monomeric precursors demonstrates self-assembly occurring during emulsion polymerization. Examples of organic and inorganic superlattices are already known but remain laboratory curiosities at the present time. Recent developments in thin-film assembly make possible preparation of superlattice molecular materials. Electrostatic self-assembly is a thin-film preparation procedure involving immersion of substrate into solutions containing charged materials. The simplicity and versatility of the electrostatic self-assembly technique allows for the preparation of new combinations of incompatible precursors. The resulting multilayer can be composed of any combination of polymers, inorganic colloids, small molecules, enzymes, and inorganic materials. If necessary, films prepared this way can be annealed to form robust films with light-emitting and electrical conducting properties. Sensor technologies could be impacted greatly by developments in the field of superlattice materials over the next few decades. The vision for the connection between superlattice materials and sensor technologies has two different directions. One relates to the potential ability of superlattices of nanostructures to bind agents from the environment, chemical or biological, with a high degree of specificity and in sufficient amounts to make detection possible. The other direction relates to the use of superlattices, organic or inorganic, as nanolithographic tools. This would impact on our ability to miniaturize complex electronic or future photonic devices to a size that makes them invisible.

## **Biomimetic Materials**

Imitation of the synthesis and processing and properties of function-integrated materials found in biological systems comprises the field of biomimetics. Recent examples include biomineralization and spider silk. Biological composites such as bones and teeth consist of a polymeric matrix reinforced by an inorganic phase. Synthetic factors comprising biomineralization include strong binding by the organic matrix of the inorganic reagents, good solvation of the

inorganic reagents by the polymer and an ordered, regular polymer environment to induce nucleation. Inorganic crystal phases normally requiring high temperatures and pressures can be prepared at room temperature and atmospheric pressure by this method. Spider silks are prepared in nature by conversion of an aqueous protein precursor solution into an oriented fiber. Imitation of this process would require preparation of cloned silk protein prepared by bacteria and conversion of precursor into fibers. Highly tensile spider silk fibers will have applications as energy-absorbing materials. Also, knowledge of silk biosynthesis has application in the synthesis of oriented polymeric fibers.

Bacteriorhodopsin is a light-sensitive protein found in halophilic bacteria. It undergoes a photocycle similar to the photocycle found in vision. Bacteriorhodopsin has been processed into thin film form and optical device concept demonstrations have been performed including dynamic holography, spatial light modulator, second-order nonlinear optical material, artificial retina and optical data storage. The wavelength sensitivity of this material can be modified by preparing tailor-made bacteriorhodopsins by genetic engineering or chemical modification of the chromophore.

### **13.3 Conclusions and Recommendations**

The field of function-integrated materials is key to materials-enabling technologies for the Air Force. The development of this field using molecularly designed nanostructures will require synthetic research aimed at finding molecular architectures that can form functional nanoparticles, both organic and inorganic. This will be important both for nanophased polymers but also in the search for superlattice materials. The mechanisms to facilitate scaleup of these new materials in order to characterize their properties will be a key element for success. The development of the area will also require finding synthetic methods for nanocomposites that accomplish molecular dispersion of polymers or organic molecules in metals, semiconductors, and ceramics.